The First Example of a d^3–d^3 Dinuclear Compound containing Four-co-ordinate Metal Atoms sharing a Pair of Bridging Ligands: $[(Bu^tO)_2W(\mu\text{-}PPh_2)]_2$

William E. Buhro, Malcolm H. Chisholm,* Kirsten Folting, Bryan W. Eichhorn, and John C. Huffman

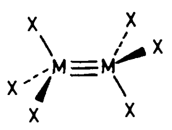
Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, IN 47405, U.S.A.

$(p\text{-Tolyl})(Bu^tO)_2W{\equiv}W(OBu^t)_2(p\text{-tolyl})$ and Ph_2PH (2 equiv.) react in hydrocarbon solvents to give toluene (2 equiv.) and $[(Bu^tO)_2W(\mu\text{-}PPh_2)]_2$ which in the solid state contains a puckered W_2P_2 moiety, W–W 2.59 Å; in solution the $W_2(\mu\text{-}PPh_2)_2$ moiety is undergoing rapid inversion on the n.m.r. time-scale.

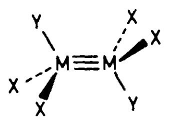
Since Wilkinson's[1] discovery of the unbridged compounds $M_2(CH_2SiMe_3)_6$, where M = Mo and W, numerous other examples of ethane-like molecules of formula $X_3M{\equiv}MX_3$, (I), or $X_2(Y)M{\equiv}M(Y)X_2$, (II), have been prepared and characterized and the chemistry of the M–M triple bond of configuration $\sigma^2\pi^4$ has been systematically developed.[2,3] Rather interestingly, not one example of the alternate structure (III), where the metal atoms are four-co-ordinate and share a pair of bridging ligands, has yet been reported. The structural type (III), is, of course, the more common in co-ordination chemistry where dimerization of two co-ordinatively unsaturated MX_3 groups occurs by bridge formation *e.g.* as in Al_2Cl_6.

The preference for structural types (I) and (II), for Mo and W, reflects the importance of M–M bonding. In (III), the fusing of two tetrahedra along a common edge can at best lead to a M–M bond of configuration $\sigma^2\pi^2\delta^2$ which, taken together with an increased M–M separation as a result of the μ-X groups, will result in a significant sacrifice of M–M bond strength. The situation is also influenced by the π-donor properties of the ligands X and Y. In (I) and (II), π-donation to the metal atoms can occur without weakening the M–M bond whereas in (III) π-donation from the terminal ligands will further weaken the M–M bond by interaction with metal d orbitals otherwise used for M–M bonding.

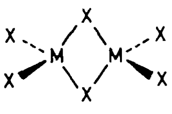
Formation of a d^3–d^3 dinuclear compound of type (III) requires the introduction of at least two ligands Y that have a high thermodynamic preference for bridging two metal atoms. They should also be significantly weaker π-donor ligands than the groups X. The compounds of formula $M_2(PR_2)_2X_4$ where M = Mo or W and X = OR or NMe_2 seemed likely to favour structural type (IIIb) over (II). A rational synthesis of such a



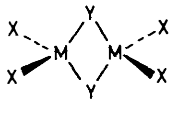
(I)



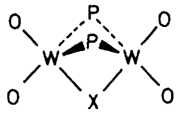
(II)



(IIIa)



(IIIb)



(IV)

compound involves the reaction between a $M_2R'_2(OR)_4$ compound,[4] which is co-ordinatively unsaturated, and a dialkyl or diarylphosphine R_2PH. We report here the first success of this synthetic strategy and our characterization of a compound of type (IIIb), namely $[(Bu^tO)_2W(\mu\text{-}PPh_2)]_2$.

Hydrocarbon solutions of (*p*-tolyl)$(Bu^tO)_2W{\equiv}W(OBu^t)_2$(*p*-tolyl) react with Ph_2PH (2 equiv.) according to equation (1) to yield dark orange solutions from which $[(Bu^tO)_2W(\mu\text{-}PPh_2)]_2$ is obtained in *ca.* 60% yield as brown crystals. The new compound, like its precursor tungsten complex, is air-sensitive and must be handled in dry and deoxygenated solvents and atmospheres (N_2). N.m.r. spectroscopy ($[^2H_8]$toluene, 22 °C) shows only one type of Bu^tO and one type of PPh_2, having equivalent phenyl rings. The ^{31}P resonance possesses satellites due to coupling to two equivalent ^{183}W nuclei, and the *ipso*-carbon atoms of the phenyl rings show both one-bond (40 Hz) and three-bond (4 Hz) couplings to phosphorus. These data† support a time-averaged molecular structure (IIIb) for $[(Bu^tO)_2W(\mu\text{-}PPh_2)]_2$, having C_{2v} symmetry.

$$1,2\text{-}W_2(p\text{-tolyl})_2(OBu^t)_4 + 2Ph_2PH \xrightarrow[\text{Hexane}]{22\,^\circ C} [(Bu^tO)_2W(\mu\text{-}PPh_2)]_2 + 2\ \text{Toluene} \quad (1)$$

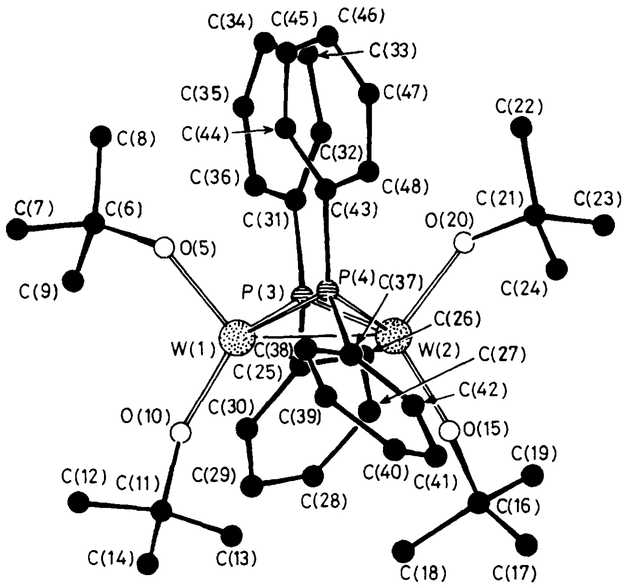


Figure 1. A ball-and-stick diagram of the $[(Bu^tO)_2W(\mu\text{-}PPh_2)]_2$ molecule viewed nearly perpendicular to the virtual O_4W_2 plane showing the puckered central W_2P_2 moiety: the dihedral angle between the P(3)–W(1)–W(2) and P(4)–W(1)–W(2) planes is 136.4°. Pertinent bond distances (Å) and angles (°) are W–W 2.591(2); W(1)–P(3), W(1)–P(4), W(2)–P(4) 2.36(1); W(2)–P(3) 2.33(1); W(1)–O(5) 1.95(1); W(1)–O(10) 1.86(2); W(2)–O(15) 1.84(2); W(2)–O(20) 1.95(2); P(3)–W(1)–P(4) 101.2(2); P(3)–W(1)–O(5) 99.7(4); P(3)–W(1)–O(10) 126.2(5); P(4)–W(1)–O(5) 92.1(4); P(4)–W(1)–O(10) 120.4(5); O(5)–W(1)–O(10) 110.4(7); P(3)–W(2)–P(4) 102.1(2); P(3)–W(2)–O(15) 119.8(5); P(3)–W(2)–O(20) 89.8(5); P(4)–W(2)–O(15) 125.0(5); P(4)–W(2)–O(20) 99.2(5); O(15)–W(2)–O(20) 113.9(7); W(1)–P(3)–W(2) 67.0(2); W(1)–P(4)–W(2) 66.6(2).

A ball-and-stick drawing of the structure found in the solid state‡ is shown in Figure 1. While the general prediction of terminal alkoxides and bridging phosphido ligands is confirmed, the molecular structure is significantly distorted from (IIIb). The co-ordination about the tungsten atoms is grossly distorted from tetrahedral. The central $W_2(\mu\text{-}P)_2$ core is puckered, not planar, and the terminal Bu^tO ligands are of two types, those with short W–O distances, 1.85 Å and large W–O–C angles, 158°, and the others with long W–O distances, 1.96 Å and smaller W–O–C angles, 128°. The local co-ordination at each metal atom may be described as a trigonal bipyramidal (tbp) fragment, WO_2P_2X, where X represents a missing axial vertex. The central $W_2O_4P_2$ unit represents two cofacial tbp WO_2P_2X units sharing a common pair of equatorial ligands, PPh_2, and a common missing axial site X. In this way O(5) and O(20), which have the long W–O distances, occupy the axial sites *trans* to the missing vertex. Diagrammatically, this is depicted by (IV).

The W–W distance of 2.59 Å is *ca.* 0.3 Å longer than those in unbridged d^3–d^3 ditungsten compounds and a simple M–M bonding description in the new phosphido-bridged compound is not viable since there must be extensive mixing of orbitals involved in M–M and M–ligand bonding. Nevertheless there must exist at least a M–M σ bond, which in terms of the fusing together of two tbp WO_2P_2X units would involve a bent M–M bond formed from overlap of d_{z^2} orbitals at the μ-X site. It seems likely that M–M bonding is responsible for the puckering of the central M_2P_2 unit. The present W–W distance of 2.59 Å is similar to that reported for the d^4–d^4 anion $W_2(\mu\text{-}Pcy_2)_3(Pcy_2)_2^-$ (cy = cyclohexyl), 2.55 Å.[6]

In related work, we have been studying the metathetical reaction shown in equation (2). For reactions involving

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† Selected n.m.r. data for $[(Bu^tO)_2W(\mu\text{-}PPh_2)]_2$: $^{31}P\{^1H\}$ (p.p.m., C_6D_6, 22 °C) 212.8 [s, $J(^{31}P\text{–}^{183}W)$ 349 Hz, satellites of 25% integral intensity], ^1H (δ, C_6D_6, 22 °C) 1.27 (s, Bu^tO); $[(NMe_2)_2W(\mu\text{-}Pcy_2)]_2$: $^{31}P\{^1H\}$(p.p.m, $[^2H_8]$toluene, 22 °C) 228.5 [s, $J(^{31}P\text{–}^{183}W)$ 305 Hz, satellites of 26% integral intensity]; ^1H (δ, $[^2H_8]$toluene, 22 °C) 3.41 (s, NMe_2).

‡ *Crystal data* for $[(Bu^tO)_2W(\mu\text{-}PPh_2)]_2$ at −157 °C: a = 11.062(4), b = 19.185(8), c = 21.969(2) Å, β = 114.51(2)°, Z = 4, D_c = 1.614 g cm^{-3} and space group $P2_1/c$. Of the 6465 reflections collected using Mo-K_α (λ 0.71069 Å) with $6 \leqslant 2\theta \leqslant 45°$ only those 2904 having $F > 3\sigma(F)$ were used in the full least-squares refinement. The W,O, and P atoms were refined anisotropically and the carbon atoms isotropically. H atoms were included at idealized fixed positions. Final residuals were $R(F)$ = 0.0529 and $R_w(F)$ = 0.0522. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

$$anti\text{-}1,2\text{-}W_2Cl_2(NMe_2)_4 + 2\ LiPR_2 \xrightarrow[\text{Tetrahydrofuran}]{-78\text{—}0\ ^\circ C} 1,2\text{-}W_2(PR_2)_2(NMe_2)_4 \quad (2)$$

LiPBu$^t_2$, we have now characterized both *anti* and *gauche* rotamers of the compound $W_2(PBu_2{}^t)_2(NMe_2)_4$.[7] The terminal phosphido ligands contain non-planar W–PC$_2$ units with W–P bond distances longer than those expected for W–P $\sigma + \pi$ double bonds. We now find that reactions employing LiPcy$_2$ lead, at low temperatures (<0 °C), to an orange crystalline compound whose n.m.r. spectroscopic properties are consistent with a structure of type (II). However, at room temperature there is a relatively slow (t_∞ *ca.* 4 h) and irreversible reaction leading to a new brown crystalline compound for which the n.m.r. spectroscopic data† are consistent with a time-averaged symmetrically-bridged structure $[(Me_2N)_2W(\mu\text{-}Pcy_2)]_2$. Thus it seems likely that a fairly extensive class of these new d^3–d^3 bridged compounds may be accessible for tungsten.

We thank the National Science Foundation and the Wrubel Computing Center for support. B. W. E. is the 1986/87 Indiana University SOHIO Graduate Fellow.

Received, 20th January 1987; Com. 074

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